BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences chimiques
Volume XXI, No. 7—8, 1973

Association Equilibria of *p*-Nitrophenol with Amines. IV. Correlation between Spectral and Thermodynamic Effects

by

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Presented by A. BASIŃSKI on February 11, 1973

Summary. UV spectral and thermodynamic effects accompanying hydrogen bond formulation of *p*-nitrophenol with triethylamine and tri-*n*-butylamine were studied, using chlorobenzene and *o*-dichlorobenzene as reaction media. The equilibrium constants of the DH+B⇄DHB reactions (DH=*p*-nitrophenol, B=base) were determined, and the associate enthalpy changes were calculated from the temperature dependences of the equilibrium constants. Deuteration of *p*-nitrophenol caused no detectable changes either in the spectra or in the thermodynamic characteristics of the hydrogen-bonded complexes. Linear correlations between ΔH and $\Delta\nu$, as well as between ΔS and ΔH, are found unique for different solvents, where $\Delta\nu$ is the red shift of the UV band of *p*-nitrophenol induced by hydrogen bond formation in the wavenumber scale, and ΔH and ΔS are the enthalpy and entropy changes of the complex formation reaction, respectively.

The equilibrium constants, as well as the associate enthalpy and entropy changes, were reported in [1, 2] for the association reactions of the type

$$\text{DH}+\text{B}\rightleftharpoons\text{DHB}, \tag{1}$$

involving *p*-nitrophenol and several aromatic amines, mainly in chlorobenzene solution (DH=proton donor, B=base). In the recent study of Hudson, Scott, and Vinogradov [3] similar data were reported for the hydrogen-bonded complexes of *p*-nitrophenol with dioxane, *n*-butylamine, and triethylamine. In order to obtain the data relating to strongly basic amines in polar media we have studied hydrogen bond formation of *p*-nitrophenol with triethylamine and tri-*n*-butylamine in chlorobenzene and in *o*-dichlorobenzene solution. In this way experimental data are completed, necessary for the study on the expected correlations between the electronic spectral and thermodynamic effects accompanying hydrogen bond formation of *p*-nitrophenol in different systems.

As it was reported in [4], absorption spectra of the hydrogen-bonded complexes of *p*-nitrophenol with tertiary amines, formed in polar media (like chlorobenzene), consist of two overlapping bands, one at approx. 225—230 nm and the other in the vicinity of 400 nm. The appearance of the latter indicates a certain degree of proton transfer within the DHB complex. It is not clear yet whether the proton

transfer consists in a thermic reaction necessitating activation energy, or in tunnelling. If the first of the two possible mechanisms actually occurred, the concept of the tautomeric equilibrium

(2) $$DH \ldots B \rightleftharpoons D \ldots HB$$

as first suggested by Bell and Barrow [5], would be applicable to the corresponding system. On the other hand, if the proton transfer consisted in tunnelling, there would be a single form of existence of the DHB hydrogen-bonded complex, whose real structure might be represented by the two limiting protonomeric structures [6]:

(3) $$DH \ldots B \leftrightarrow D \ldots HB.$$

It seemed probable that a DHB complex, being an equilibrium mixture of two tautomeric modifications, might differ markedly in its thermodynamic characteristics from that in which the same degree of proton transfer due to tunnelling occurs. With this in view, the equilibrium constants and other thermodynamic parameters have been determined for the ordinary and the deuterated *p*-nitrophenol. It was expected that the substitution of deuteron for proton might reduce the tunnelling mechanism of particle transfer if the two mechanisms were about equivalent in the protonated complex.

Experimental

Purification of materials and other experimental procedures were as those described in [4]. Deuterated *p*-nitrophenol, obtained from the Institute of Organic Chemistry of the Polish Academy of Sciences, Warsaw, was dried by prolonged storing in a dessicator over potassium hydroxide and used without further purification.

Results and discussion

A series of spectra corresponding to a constant concentration of *p*-nitrophenol and a number of different concentrations of triethylamine in chlorobenzene solution was reported in [4]. The results presently obtained for solutions in *o*-dichlorobenzene are similar in that the spectrum of the hydrogen-bonded complex with maximum at 328.5 nm exhibits a shoulder indicating a second overlapping band in the vicinity of 400 nm. An isosbestic point in the set of absorption curves is also observed, indicating a single equilibrium of type (1). This conclusion is additionally supported by the fact that at a certain concentration of the amine the limiting spectrum corresponding to the complete transformation of *p*-nitrophenol into the hydrogen-bonded complex is obtained (Fig. 1). It is only at considerably higher amine concentrations that further changes in the spectrum occur, corresponding to not so well-defined equilibria. They have not been studied here.

Spectral effects accompanying hydrogen bond formation of *p*-nitrophenol with tri-*n*-butylamine in chlorobenzene and *o*-dichlorobenzene solutions (Figs. 2 and 3) are similar to those found for the corresponding systems involving triethylamine. The difference consists in different dependences of the spectral changes

on the concentration of the amine, considerably higher concentrations of the amine being necessary for the complete transformation of *p*-nitrophenol into the complex. It is to be noted, however, that the present results indicate but a small degree of

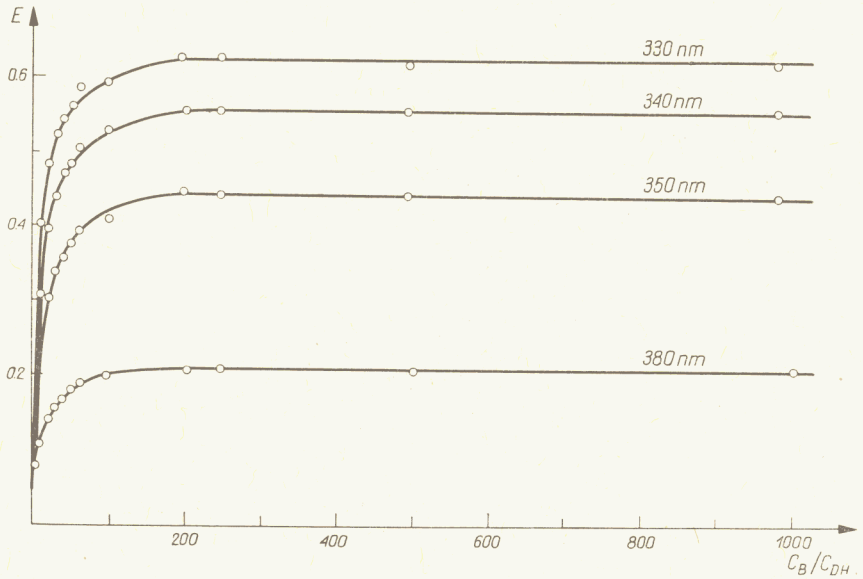

Fig. 1. Dependences of the optical densities of the *p*-nitrophenol (6.29×10^{-5}M)+triethylamine solutions in chlorobenzene on the concentration ratio of the base (B) and the proton-donor (DH); 20°C

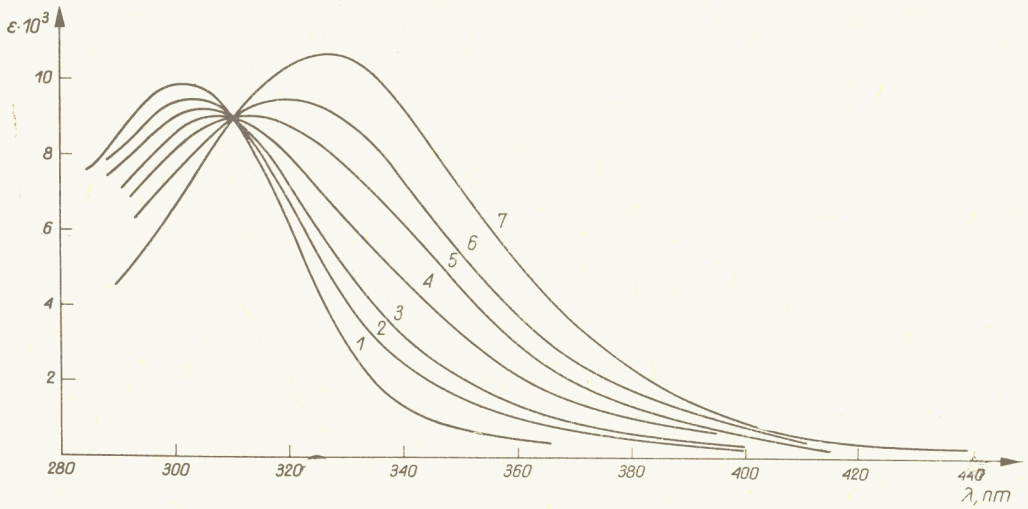

Fig. 2. Absorption spectra of the *p*-nitrophenol (6.21×10^{-5}M)+tri-*n*-butylamine (concentration variable from 0, curve 1, to 0.07×10^{-2} M, curve 7) solutions in chlorobenzene; 20°C

proton transfer within the DHB complex involving tri-*n*-butylamine in chlorobenzene solution. No detectable differences in the spectra have been observed between the systems involving deuterated and non-deuterated *p*-nitrophenol.

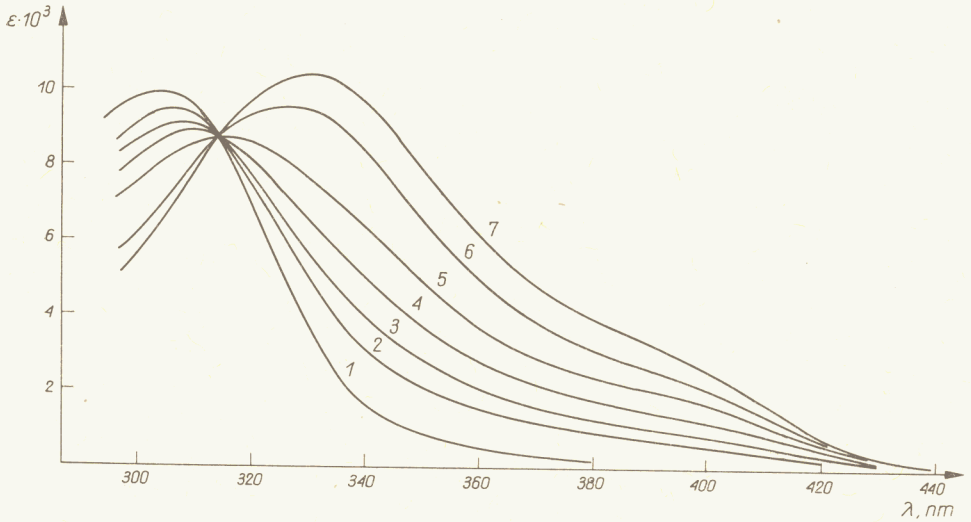

Fig. 3. Absorption spectra of the *p*-nitrophenol (6.29×10^{-5} M)+tri-*n*-butylamine (concentration variable from 0, curve *1*, to 9.28×10^{-2} M, curve *7*) solutions in *o*-dichlorobenzene; 20°C

Apart from the question whether the DHB hydrogen-bonded complex is a single species of an equilibrium mixture of two structural modifications differing in the position of the proton, in equilibrium studies it behaves as a single complex whose equilibrium constant can be determined by standard spectrophotometric methods. Here the well-known Rose—Drago method [1] has been used to evaluate the spectrophotometric data. The resulting values of the equilibrium constants for the type (1) reactions determined at 20°, 25°, and 30°C, are listed in Table I. To determine whether or not deuteration of the phenolic group of *p*-nitrophenol will result in a detectable change in the thermodynamic characteristics of the DHB complex involving the strong bases in polar media an entirely new series of experiments involving new materials has been performed. In these new experiments the equilibrium constants for the protonated and deuterated *p*-nitrophenols have been determined in parallel, identically performed experiments. As a result, a new series of data for the non-deuterated complexes have been obtained, differing within the experimental error from the older ones. In Table I we report both, as they confirm the reliability of the data. The other thermodynamic parameters, ΔH and ΔS, for the reactions of type (1) were calculated as usually, while making use of the temperature dependences of the equilibrium constants.

In Table I are collected the basic spectral characteristics, λ_{max} and ε_{max} of the hydrogen-bonded complexes of *p*-nitrophenol formed in the systems studied, along with the derived thermodynamic parameters, K, ΔH, and ΔS. Inspection of the data shows that the deuterated and non-deuterated complex of *p*-nitrophenol,

TABLE I

Spectral and thermodynamic characteristics of the hydrogen-bonded complexes of *p*-nitrophenol and deuterated *p*-nitrophenol with different amines in chlorobenzene and *o*-dichlorobenzene solution

	Reacting system	Solvent	λ_{max} nm	ε_{max}	K, mol^{-1} dm^3			ΔH_{298} $kcal/mol^{-1}$	ΔS_{298} cal/mol^{-1}
					20°C	25°C	30°C		
1	PNP—pyridine	chlorobenzene		11070	310	250	200	7.7	15.0
			317.5	11050	310	—	199	7.8	15.2
2	PNP(d)—pyridine			11080	311	—	200	7.8	15.2
3	PNP—pyridine	*o*-dichlorobenzene		11200	520	385	322	8.4	16.4
			320	11210	519	—	320	8.5	16.7
4	PNP(d)—pyridine			11190	510	—	318	8.4	16.2
5	PNP—triethylamine	chlorobenzene		10430	1000	720	550	10.5	22.3
			324.5	10430	985	—	560	10.0	20.3
6	PNP(d)—triethylamine			10290	1015	—	565	10.3	21.4
7	PNP—triethylamine	*o*-dichlorobenzene		10000	1550	1050	800	11.6	24.9
			328.5	10000	1530	—	804	11.4	24.2
8	PNP(d)-triethylamine			9995	1560	—	807	11.6	25.0
9	PNP—tri-*n*-butylamine	chlorobenzene		11510	320	260	220	6.6	11.0
			326	10670	321	—	219	6.8	11.7
10	PNP(d)—tri-*n*-butylamine			10610	321	—	220	6.7	11.4
11	PNP—tri-*n*-butylamine	*o*-dichlorobenzene		10300	435	355	270	9.3	19.6
			328	10420	431	—	261	8.8	18.0
12	PNP(d)—tri-*n*-butylamine			10300	425	—	263	8.5	16.8

not only with the relatively weak amines like pyridine, but also with stronger ones, forming complexes with a marked degree of proton transfer, display the same (within the experimental error) spectral and thermodynamic characteristics. This may be due to the fact that on passing from the non-deuterated to the deuterated *p*-nitrophenol no change in the nature of the particle transfer occurs. No argument in favour of any of the two possible interpretations of the proton transfer, observed in the systems involving triethylamine and tri-*n*-butylamine in the two polar solvents, chlorobenzene and *o*-dichlorobenzene, can therefore be obtained in this way.

Apart from the above question as to the nature of proton transfer within some of the DHB complex of *p*-nitrophenol, the present results together with the previous ones provide a good basis for the study on the correlations between the spectral and thermodynamic effects accompanying hydrogen bond formation of *p*-nitrophenol. The relevant data are collected in Table II. In the second column

TABLE II

Spectral and thermodynamic characteristics of hydrogen-bonded complexes of *p*-nitrophenol at 25°C

	Base (pK_b)	Solvent	$\Delta\nu$ cm^{-1}	K_{298} $mol^{-1}\,dm^3$	ΔH kcal	ΔS cal/K^{-1}	Ref.
1	2-chloropyridine (13.28)	chlorobenzene	1320	19(±3)	6.1	14.5	[2]
2	3-chloropyridine (11.16)	chlorobenzene	1470	54(±3)	7.2	16	[2]
3	pyridine (8.77)	benzene	1690	116(±5)	6.8	13	[1]
4	pyridine	chlorobenzene	1770	250±10	7.8	15.2	—
5	pyridine	*o*-dichlorobenzene	1850	385±10	8.4	16.4	—
6	2-methylpyridine (8.03)	chlorobenzene	1820	375(±10)	8.5	17	[2]
7	3-methylpyridine (8.32)	chlorobenzene	1870	396(±10)	8.6	17	[2]
8	triethylamine (3.27)	chlorobenzene	2400	270(±10)	10.3	21.4	—
9	triethylamine	*o*-dichlorobenzene	2650	1050(±10)	11.5	24.7	—
10	tri-*n*-butylamine (3.17)	chlorobenzene	2400	260(±10)	6.7	11.4	—
11	tri-*n*-butylamine	*o*-dichlorobenzene	2380	355(±10)	8.7	17.8	—
12	dioxane	cyclohexane	1300	—	7.03 (±0.84)	15.5 (±3.1)	[3]
13	*n*-butylamine	cyclohexane	2180	—	9.21 (±0.63)	16.0 (±2.3)	[3]
14	triethylamine (3.27)	cyclohexane	2390	—	10.3 (±0.41)	20.6 (±1.5)	[3]

of Table II are listed the amines acting as the bases in the type (1) reactions with the values of their basicity constants (relating to aqueous solution) indicated. For most of the amines the equilibrium constants have been determined in chlorobenzene solution, while for some of them the data relating to benzene and *o*-dichlorobenzene as the reaction media have also been obtained, as indicated in the third column.

Included are the data of Hudson *et al.* [3] relating to cyclohexane. The fourth column contains the spectral shifts $\Delta\nu$, defined as $\Delta\nu = \nu_b - \nu_f$, where ν_b and ν_f are the positions of the bands due to the hydrogen-bonded and free *p*-nitrophenol, respectively, in the wavenumber scale. For the three solvents studied, viz., benzene, chlorobenzene, and *o*-dichlorobenzene, the determined values of ν_f are 33500, 33200, and 33000 cm^{-1}, respectively. The method used for the determination of the position of the bands was described in [2]. The uncertainty in the quoted values of the spectral parameters is estimated as $\pm 50\ cm^{-1}$, corresponding to ± 0.5 nm in the wavelength scale. In further columns of Table II are listed the values of the enthalpy change (ΔH), and the entropy change (ΔS) of the reactions considered, relating to 25°C. The uncertainty in ΔH is estimated as ± 0.5 kcal, while that in ΔS as ± 1.5 cal K^{-1}. For the systems involving pyridine, ethylamine, and tributylamine in chlorobenzene as well as in *o*-dichlorobenzene solution, for which two sets of experimental data have been obtained, the mean values of ΔH and ΔS are given in Table II.

Inspection of the data listed in Table II shows that the negative enthalpies of the type (1) reactions increase, in general, with the increasing red shift of the band induced by hydrogen bond formation. This agrees with what might be expected on purely speculative grounds, while taking into account the basic relation

$$hc\Delta\nu = \Delta H_e - \Delta H \tag{4}$$

where ΔH_e and ΔH are the enthalpy changes of the type (1) reactions taking place in the excited Franck—Condon state and in the ground state, respectively. It may be assumed that $\Delta H_e > \Delta H$ and, consequently, $\Delta\nu < 0$ for those excited states in which the proton donating power of the OH group is higher than in the ground state. The fact that $\Delta\nu < 0$ for the UV band of *p*-nitrophenol clearly indicates that the OH bond in the corresponding excited state is more polar than in the ground state, obviously as a result of the reduction in the π-electron density at the oxygen atom brought about by the electronic transition. This agrees with the simplified interpretation of the band as being due to the intramolecular charge-transfer [6]. It seems reasonable to assume that ΔH_e, the energy of the hydrogen bond formed in the excited Franck—Condon state, be proportional, in the first approximation, to ΔH, the energy of the bond formed in the ground state with the same base in the given solvent. Thus, putting $\Delta H_e = k\Delta H$ in Eq. (4) we obtain

$$\Delta H = a \cdot \Delta\nu \tag{5}$$

where $a = hc/(k-1)$. Fig. 4 provides a check on this expected relation. The majority of experimental points (open circles) correspond to chlorobenzene as the reaction medium, while the rest relate to benzene or *o*-dichlorobenzene. The data of Hudson *et al.* [3], relating to cyclohexane, have also been indicated. Inspection of Fig. 4 shows that the dependence of $-\Delta H$ on $-\Delta\nu$ may satisfactorily be approximated by a straight line having zero intercept, in accordance with the above expectation. The relation simply reflects the fact that ΔH_e and ΔH increase or decrease in a constant proportion on passing from one system to another. However, unex-

pected is the fact that the correlation seems to be unique for the group of solvents, to which the data relate, including cyclohexane. Thus it may be noted that on passing from cyclohexane to benzene, chlorobenzene, or *o*-dichlorobenzene the position

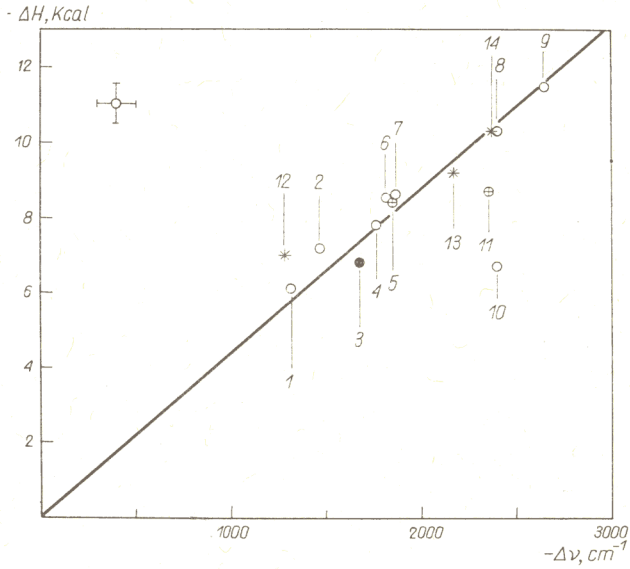

Fig. 4. Correlation between $-\Delta H$ and $-\Delta\nu$ of the type (1) reactions involving *p*-nitrophenol and different amines in different media

Benzene (●), chlorobenzene (○), *o*-dichlorobenzene (⊕), and cyclohexane (∗) solution. For the notation of the points see Table II

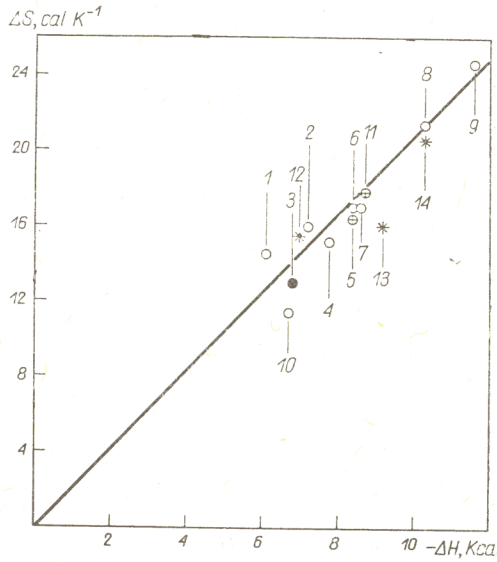

Fig. 5. Correlation between ΔS and ΔH of the type (1) reactions involving *p*-nitrophenol and different amines in different media

The notation of the points the same as in Fig. 4

of the band being due to either free or hydrogen-bonded *p*-nitrophenol changes significantly, indicating marked changes in the interaction between the solute and the solvent.

Another interesting observation is that the negative entropies of the type (1) reactions also increase with either the increasing red shift of the band under consideration or the increasing energy of the hydrogen bond, as characterized by the value of ΔH. Fig. 5 shows the plot of ΔS vs. $-\Delta H$ for the type (1) reaction of *p*-nitrophenol. Again, the correlation seems to be linear and unique for different solvents. It can be noted that the negative entropies are in general smaller than the expected value of approx. 25 e.u. for the purely translational contribution to the overall entropy change of the type (1) reactions. If the observed variations in the entropy of this reaction with varying nature of the amine were due to solvation effects, the correlation between ΔS and ΔH could not be unique for different solvents, especially when they differ in polarity. Therefore, it seems more probable that the variations in the entropies of the type (1) reactions of *p*-nitrophenol are determined by some internal degrees of freedom closely related to the strength of the hydrogen bond in the DHB complex. However, for a fuller understanding of the significance of the two correlations found in this work, further study seems to be necessary.

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В. Либусь, З. Даутэр, В. Моска, **Ассоциационные равновесия *p*-нитрофенола с аминами. IV. Корреляции между спектральными и термодинамическими эффектами**

Содержание. Исследованы спектральные эффекты в ультра-фиолетовой части спектра, а также термодинамические эффекты сопутствующие образованию водородной связи между *p*-нитрофенолом с триэтиламином, а также три-*n*-бутиламином в среде хлорбензола и *o*-дихлорбензола. Определены константы химического равновесия реакции DH+B⇄DHB (DH=*p*-нитрофенол, B=основание), а соответствующие им константы равновесия были вычислены из температурных зависимостей констант равновесия. Констатировано, что дейтерация *p*-нитрофенола не вызывает заметных изменений так в электронных спектрах, как и в термодинамических величинах образующихся комплексов. Констатировано также существование линейной корреляции между ΔH и $\Delta\nu$, и между ΔH и ΔS, той-же самой для разных растворителей, где $\Delta\nu$ обозначает перемещение в направлении меньших частот ультрафиолетовой полосы *p*-нитрофенола вызванное образованием водородной связи, тогда как ΔH и ΔS являются соответственно изменением энтальпии и изменением энтропии вышеприведенной реакции.